A Study of the Determination of Hydrogen by Absorption in Liquid Reagents

BY

DONALD T. BONNEY

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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A Study of the Determination of Hydrogen by Absorption in Liquid Reagents

TECHNICAL methods of gas analysis for the determination of hydrogen in general use in the United States depend almost universally upon procedures employing explosion or combustion. Of these, the fractional combustion over copper oxide (*6*, *7*, *16*, *17*, *20*, *21*, *25–29*, *31*) or the "slow combustion" (*9*, *10*, *18*, *30*) over a glowing platinum spiral is generally preferred. The chief disadvantage of the copper oxide method is the time required for the determination, during which the operation must be constantly attended.

The "slow combustion" method, while accurate under proper control, is not satisfactory when more than one hydrocarbon is also present in the mixture, and is generally restricted to the determination of methane and ethane. The manipulations required are exacting and the danger of an explosion must constantly be guarded against.

While a number of absorption methods involving liquid reagents have been proposed, the use of these has been limited. Dilute palladium chloride solutions (*8*, *24*), sodium oleate solutions containing finely divided activated nickel (*1*, *3*), sodium chlorate solutions in contact with a palladium activator (*13*, *14*, *15*), and silver permanganate solution (*11*) have been suggested. The reactions involved have, however, generally been deemed slow or unsatisfactory or the preparation of the reagent and apparatus troublesome and expensive.

Among the methods previously advanced, the most satisfactory appears to be that of Paal and Hartman (*23*), who employed a sodium picrate solution containing a very active and stable palladium colloid (*22*). In accuracy, it has been shown by a number of investigators (*2*, *4*, *5*, *12*) to be equal or superior to combustion methods. It is, however, time-consuming, a single determination requiring as high as 30 minutes. Furthermore, the absorbent is expensive, because of the high palladium colloid content, and with high concentrations of hydrogen it is soon spent. Brunck (*4*) suggested the use of a higher sodium picrate content, and also advanced a method for recovering the palladium catalyst from the spent solution.

For simplicity and ease of operation, an automatic pumping pipet has been developed in the laboratories of this department. This frees the operator from the necessity for con-

stant vigilance and so minimizes the objections raised against the time required, and by setting up more favorable contact conditions between the solution and the gaseous mixture increases the rate of absorption. These desirable features suggested the use of reagents hitherto considered too sluggish to be practicable and so directed attention to the determination of hydrogen by liquid reagents.

While the method of Paal and Hartman (*23*) appeared to be the most satisfactory of those hitherto advanced, it was soon recognized that it would be desirable to replace the sodium picrate with a substance having a higher rate of absorption and having also the property of being readily reoxidized to its original form without affecting the palladium catalyst, thereby giving a much longer life.

Preliminary Experiments

A rapid preliminary study, largely qualitative in nature, was made on a variety of materials. Among the inorganic substances, sodium metavanadate catalyzed by colloidal palladium showed some activity. To this mixture other metals were added, including silver, cerium, thorium, molybdenum, tungsten, uranium, and manganese. Molybdenum solutions when used alone gave some promise. A ferric citrate–colloidal palladium solution showed an absorption slightly greater than did the palladium colloid alone.

The colloid used was a sodium protalbinate–palladium colloid prepared in a manner essentially similar to that of Paal and Amberger (*22*).

Preparations

Sodium Protalbinate. Fifty grams of powdered egg albumin were added slowly with stirring to 250 cc. of a 3.0 per cent sodium hydroxide solution. The mixture was heated at 95° to 100° C. on a water bath with occasional stirring, until practically all the albumin had dissolved. During this digestion considerable ammonia was evolved. The solution was filtered to remove impurities, chiefly inorganic salts. The filtrate was then made slightly acid with 6 *N* acetic acid, the protalbinic acid being precipitated. After settling for 12 hours the precipitated protalbinic acid was made into a thin paste with water and dialyzed for 3 days with distilled water in a Cellophane sack.

The purified protalbinic acid was dissolved by the addition of excess sodium hydroxide solution and again dialyzed until neutral to litmus. The resulting sodium protalbinate solution was evaporated to a small bulk at 60° to 70° C. and then precipitated and freed from water by several successive additions of 95 per cent alcohol. The sodium protalbinate was further dried in a desiccator. Yield, 14.6 grams or 29.2 per cent.

Sodium Protalbinate–Palladium Colloid. Three grams of sodium protalbinate were dissolved in 50 cc. of water and sufficient sodium hydroxide was added to combine with the chlorine of the palladium chloride. The palladium chloride solution, containing 4 grams of palladium chloride (2.0 grams Pd) in 70 to 80 cc. of water, was added slowly while stirring. A yellow-red precipitate first formed but redissolved. An excess of hydrazine was added drop by drop while stirring and the solution was then allowed to stand for several hours. The

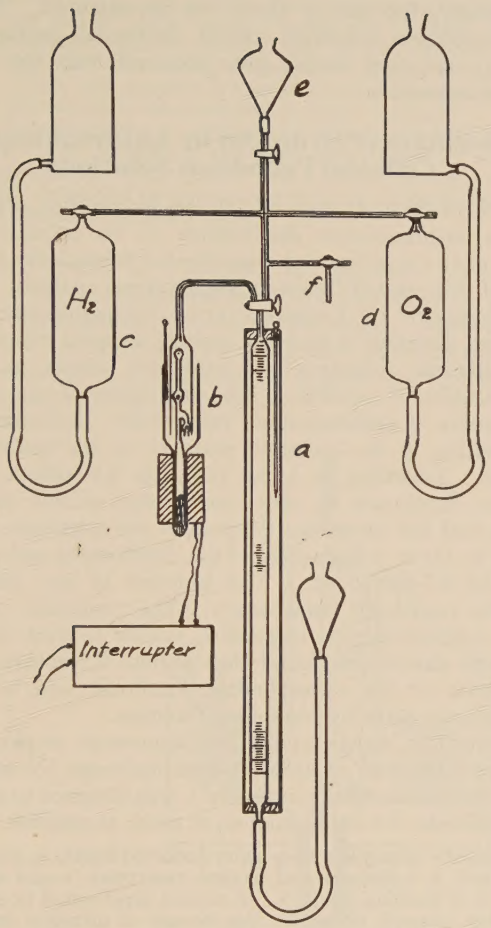

FIGURE 1. APPARATUS FOR ACTIVITY TESTS

resulting solution was dialyzed with distilled water in a Cellophane sack until neutral to litmus and free from chlorides. During dialysis the solution increased in volume considerably because of osmosis. The colloid, thus freed from salts, was evaporated to dryness at 60° to 70° C. and further dried in a desiccator.

The palladium colloid preparation was obtained in the form of glistening black plates, soluble in water and alkaline solutions.

Early in the investigation, it was recognized that organic compounds having a quinoid structure might prove satisfactory, because of their ability to shift readily back and forth between the quinone and the hydroquinone forms on alternate oxidation and reduction. A serious difficulty in the use of the simple quinones is their extremely low solubility in water. However, 1,2-naphthoquinone and a number of the anthraquinone sulfonates are soluble to some extent.

Accordingly, the use of these was investigated. The 1,2-naphthoquinone solutions tested decreased gradually in activity, but good results were obtained with the anthraquinone sulfonates.

Absorption of Hydrogen by Anthraquinone–Colloidal Palladium Solutions

As the preliminary tests had shown the solution containing sodium anthraquinone disulfonates to be promising, the course of the investigation was directed toward the development of this reagent for use in standard gas analysis.

Preparation of Anthraquinone Disulfonates. It is, of course, desirable to have the organic material which undergoes alternate reduction and oxidation present in a high concentration if possible. The solubilities of the various disulfonates of anthraquinone vary widely, depending upon the position in the molecule assumed by the sulfonic acid radicals. According to Lauer (*19*), the 2,7-sodium anthraquinone disulfonate is very much more soluble than the others, and the procedure followed in the synthesis was designed to favor a high yield of the disulfonates and particularly the 2,7-compound. The isolation of any particular salt was considered unnecessary. The procedure followed in the sulfonation was, in general, similar to that of Lauer. At a later date it was found that sodium 2,7-anthraquinone disulfonate or the corresponding disulfonic acid is offered in an impure state by commercial sources.

Absorption Apparatus. The apparatus employed for measuring the rate of absorption of hydrogen by solutions, shown diagrammatically in Figure 1, was designed to simulate the conditions of routine analysis as much as possible.

It consists essentially of a water-jacketed buret, *a*, an absorption pipet, *b*, hydrogen and oxygen reservoirs, *c* and *d*, and a reservoir of flushing liquid, *e*. A second pipet could be attached at *f* when desired, either for the storage of nitrogen or for the absorption of gases other than hydrogen. Acidulated salt water was used as the flushing liquid and as the confining liquid in the buret.

As previously mentioned, the usefulness and convenience of procedures for the analytical absorption of hydrogen in liquid reagents had been enhanced by the development of an automatic pumping pipet. Accordingly, the determinations were usually made in a pipet of this kind, shown diagrammatically in Figure 2.

The pumping mechanism consists of the solenoid, *a*, glass-enclosed iron plunger *b*, valves *c* and *c'*, spray bulb *d*, and timing device *e* to make and break the circuit of the solenoid. When the circuit to the solenoid is closed the plunger rises, forcing the reagent up through tube *f*. Valve *c* is forced shut, *c'* opens, and the reagent is sprayed against the walls of the pipet. When the current to the solenoid is broken the plunger falls, valve *c'* closes, and *c* opens, allowing fresh reagent to be drawn in above the plunger. The removal of solutions and cleansing of the pipet were facilitated by constructing the pipet in three sections.

Upon removal of the top section, the pumping mechanism can be lifted out and all parts readily drained and washed. During the study of the effect of temperature on the activity of the reagent, the pipet was cooled or heated by means of the water bath, *h*. Heat was supplied by an immersion heater consisting of a coil of resistance wire enclosed in Pyrex tubing.

When it was desired to operate out of contact with air, the upper and lower sections of the pipet were sealed by a rubber ring containing the thermometer and a rubber gas bag, such as is generally employed to prevent access of air to the back chamber of the usual absorption pipet.

Determination of Activity of Reagent. The production of the crude disulfonates of anthraquinone by laboratory syntheses gives a mixture of compounds. Accordingly, a number of preparations were made and examined to obtain as active a solution as conveniently possible and to determine the duplicability of the results.

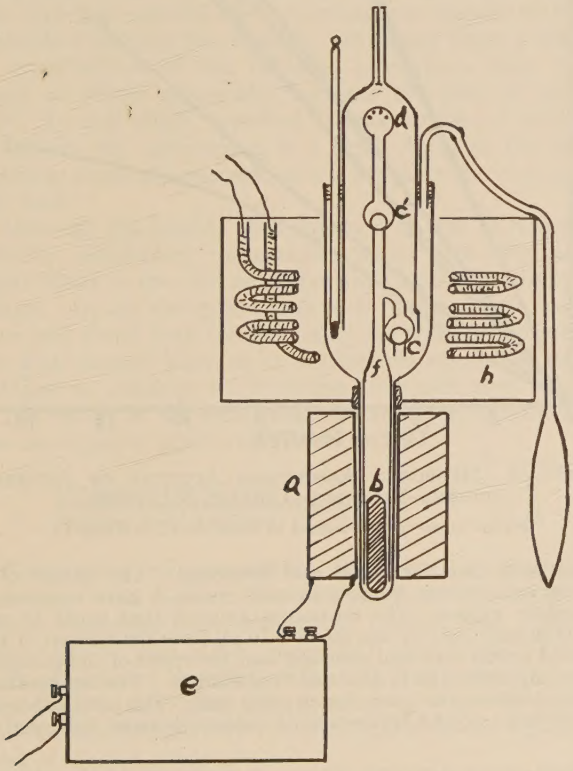

Figure 2. Pipet for Activity Tests

The values for the sodium anthraquinone disulfonate content include soluble impurities which may result from the preparation, including, of course, important amounts of sodium chloride. The tests were carried out as follows:

The sample of hydrogen, usually about 100 cc., was measured in the buret and 50 cc. were then transferred to the absorption pipet. The pipet was closed, a stop watch started, and the circuit for the pumping device closed. After 4 minutes, the pumping action was stopped and the unabsorbed hydrogen

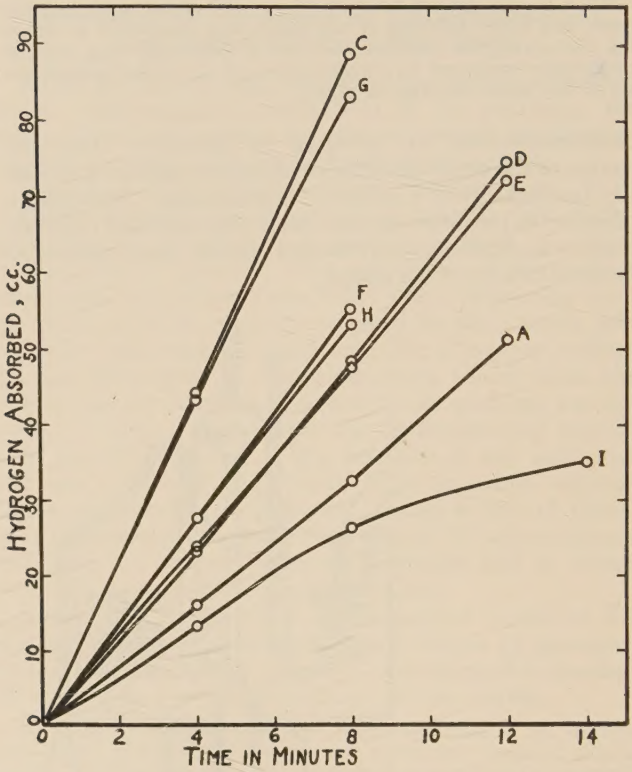

FIGURE 3. HYDROGEN ABSORPTION ACTIVITY OF ANTHRAQUINONE–PALLADIUM COLLOID SOLUTIONS

(Letters on curves correspond to those shown in Table I.)

drawn back into the buret and measured. The period of 4 minutes was chosen because in most cases it gave convenient absorption values. The maximum amount that could be absorbed in any one run was 50 cc. In all tests the current of the solenoid circuit was held constant and the speed of the pumping action adjusted to 33 to 34 strokes per minute. The temperature of the solution was read during each run. The solutions were revivified by oxygen between tests unless otherwise indicated.

SUMMARY OF ACTIVITY TESTS. A summary of the absorption rates of tests of a number of solutions prepared is shown in Table I. In order to present the data as briefly as possible, only one value of the absorption rate for each solution is given. The value selected is that for the maximum rate which was obtained at a temperature approaching as closely as possible 25° C. The low absorption values for solutions

D, F, E, and A are probably due to high sodium chloride content in the anthraquinone, resulting in false values for the weight of sodium anthraquinone disulfonate. Moreover, the composition of the colloidal palladium employed in some of the earlier solutions was doubtful, as trouble was sometimes experienced in securing a completely soluble product.

The activity of the solutions given in Table I is shown graphically by Figure 3, in which the volume of hydrogen absorbed is plotted against the absorption time.

Comparison of Absorption Rates with Pumping and Bubbling Pipet. As indicated, this reagent was intended primarily for use with the pumping pipet employed in the tests of Table I. However, because of the limited extent to which this type of pipet has been applied, a comparison of the absorption rates of the anthraquinone reagent in a pipet more generally employed should be of interest. As the bubbling pipet is commonly employed in technical gas analysis, this type was selected for the comparison (similar to Fisher Scientific Company No. 10-645). In recent years a number of modifications of the bubbling pipet have been made, many of which appreciably increase the rate of absorption. In this study, however, it was considered advisable to restrict the comparison to a single type, so the simple bubbling pipet was selected, as it is probably the most generally used.

Although the reagent used (solution F) was of rather low activity, satisfactory comparative values were obtained, as slight errors in time did not appreciably affect the absorption values. In the absorption tests with the bubbling pipet the time was noted both for the actual bubbling period and for the total elapsed time, as an appreciable amount of time is required to withdraw the hydrogen after each pass.

The results of the comparison of the absorption rate with the two types of pipet were as follows:

	Cc./min.
Automatic pumping pipet	4.76
Bubbling pipet, actual bubbling time	3.85
Bubbling pipet, total time	2.30

Comparison of Absorption Rate of Anthraquinone Reagent with Sodium Picrate Reagent. Although the sodium anthraquinone disulfonate reagent was developed principally to give a life longer than that of the Paal and Hartman reagent by virtue of the fact that it may be readily reoxidized, it also offers the advantage of a greater activity. This is demonstrated by the comparison of the absorption rates of the two solutions:

	Cc./min.
Anthraquinone reagent (solution C)	9.30
Paal and Hartman's sodium picrate reagent	2.85

Variation of Activity with Temperature. An increase in the activity of the reagent with increasing temperature was to be expected from the behavior of palladium black and

the sodium picrate–palladium colloid solution of Paal and Hartman. The variation of activity with temperature was studied over the range of 10° to 35° C. employing two reagents (solutions C and F). In this range the increase of activity averaged 2.8 cc. or 26 per cent per 10° temperature rise. A decrease in activity was noted in each case after heating to above 35° C. Upon subsequent removal of the solutions, a portion of the palladium was found to have precipitated, indicating that the reagent becomes unstable at 35° to 40° C. This is, however, no serious disadvantage for, although the activity does increase with temperature, the rate of increase hardly warrants the complication and expense required when means for heating the solution is introduced.

Determination of Hydrogen in Gas Mixtures

In order to establish the value of the anthraquinone–palladium colloid reagent, the behavior of the reagent toward mixtures of hydrogen with the various other gases commonly encountered in technical analysis was next examined. These mixtures included hydrogen and oxygen, hydrogen and nitrogen, hydrogen and saturated hydrocarbons, hydrogen and carbon monoxide, and hydrogen and carbon disulfide.

TABLE I. SUMMARY OF ACTIVITY TESTS

Solution	Composition: Sodium anthraquinone disulfonate	Palladium	Maximum H_2 Absorption Rate	Temp.
	Grams	*Grams*	*Cc./min.*	*° C.*
C	15.0	1.0	11.07	23.5
G	16.0	1.0	10.44	29.5
D	18.7 (NaCl?)	0.7	6.23	26.0
F	38.0 (NaCl?)	1.8	6.68	27.5
E	10.0 (NaCl?)	0.7	6.01	24.3
A	8.0 (NaCl?)	0.7	4.21	25.0
H	9.0 grams sodium nitro anthraquinone sulfonate	1.9	6.50	23.0
I	(Pd alone)	1.0	3.30	29.0

HYDROGEN AND OXYGEN. Hydrogen and oxygen are simultaneously absorbed by the anthraquinone reagent at a rate higher than their individual absorption rates. In the case of detonating gas ($2H_2 + O_2$) the rate is extremely rapid and no change takes place in the anthraquinone reagent. Unless the concentration of one of them is known, however, determinations of a mixture of hydrogen and oxygen can give only the total content of both gases. The simultaneous absorption of hydrogen and oxygen may be advantageous in certain procedures.

HYDROGEN AND NITROGEN. The determination of hydrogen in hydrogen-nitrogen mixtures of varying composition is shown in Figure 4. The determinations were made employing the most active solutions, C and H, which had been prepared according to the method adopted as being the most

satisfactory. The time necessary for the determination of hydrogen in gaseous mixtures varies from about 2 minutes for low concentrations up to 10 minutes for a concentration of 50 per cent. For the usual gaseous mixtures encountered in routine analysis, the hydrogen concentration is seldom much above 50 per cent.

TABLE II. ANALYSES OF NATURAL GAS

	Hydrogen Found by		
	Anthraquinone–palladium colloid reagent		Copper oxide tube (Bureau of Mines apparatus)
	%	%	%
C_nH_{2n}	0.8	1.0	0.8
O_2	0.8	1.0	1.0
H_2	3.0	3.0	2.9
C_nH_{2n+2} and N_2	95.4	95.0	95.3

HYDROGEN AND SATURATED HYDROCARBONS. In technical gas analysis, in accordance with the usual sequence, the hydrogen would be determined in the presence of saturated hydrocarbons and nitrogen. The behavior of the reagent with hydrogen-saturated hydrocarbon mixtures was therefore examined. From analogy with the behavior of the Paal and Hartman solution it was expected that the anthraquinone reagent would be satisfactory for the determination of hydrogen in the presence of saturated hydrocarbons.

This was verified by the results shown in Table II, using in one case the anthraquinone reagent for the hydrogen determination in natural gas and in the other the fractional combustion of the same gas mixture over copper oxide.

Effect of Carbon Monoxide and Carbon Disulfide on the Activity of Reagent

Carbon monoxide and organic sulfur compounds are important catalyst poisons frequently present in industrial gases. Accordingly, the effect of the presence of carbon monoxide and carbon disulfide upon the activity of the reagent was investigated. The results of this study may be briefly summarized as follows:

CARBON MONOXIDE. (1) Hydrogen and carbon monoxide may be removed simultaneously by the anthraquinone–palladium colloid reagent. (2) The absorption rate is extremely slow because of the poisoning effect of carbon monoxide. (3) Upon complete revivification with oxygen the reagent regains its original activity.

CARBON DISULFIDE. Carbon disulfide acts as a powerful poisoning agent for both the absorption of hydrogen and the subsequent revivification with oxygen. However, after standing in contact with air for a period of from 2 to 3 weeks the reagent regains its original activity. A concentration (2.3 per cent) of carbon disulfide very much higher than that found in gases for public utility work was employed in this test to exaggerate the effect of the low concentrations in industrial gases.

Capacity, Life, and Revivification of Reagent

CAPACITY. Although the reagent has the advantage of being readily reoxidized by contact with oxygen or air, it

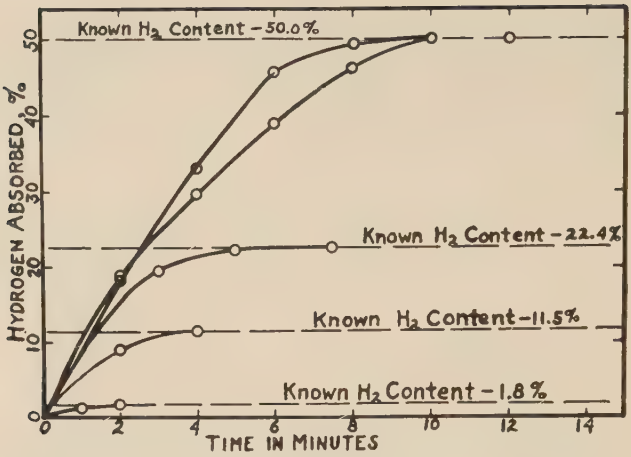

FIGURE 4. ANALYSES OF HYDROGEN-NITROGEN MIXTURES, SOLUTION C

is necessary for it to have some capacity for absorbing hydrogen. The greater the capacity, of course, the greater will be the number of hydrogen determinations possible before revivification becomes necessary. A test was therefore carried out to determine the volume of hydrogen that could be absorbed before the solution became too sluggish for use. During this test the reagent was sealed from the atmosphere by the rubber ring and gas bag previously mentioned. The volume of the reagent was 120 cc.

The results of this test are shown in Figure 5. It is seen that the hydrogen absorption rate is still satisfactory after 800 cc. have been absorbed.

REVIVIFICATION AND LIFE OF THE REAGENT. The revivification of the anthraquinone reagent by oxygen or air has been mentioned frequently. Some data showing the rate and completeness of the revivification are of interest, as it affects so greatly the life, and thereby the economy, of the reagent. The rate of revivification, as would be expected, varies with the amount of the reduced material present and the oxygen concentration. During the determination of the hydrogen absorption rates under the various conditions set up in the study of the reagent, the solutions were kept in a highly oxidized state in order to eliminate the effect of the degree of reduction. Under this condition, not necessary in practice, the revivification proceeds rather slowly. It may be said, conservatively, that with a corresponding state of reduction, the rate of oxygen absorption during revivification is as great as that of hydrogen absorption, and probably exceeds it. Apparently, the influence of the hydrogen-ion concentration upon the rate of revivification is also important.

That complete revivification may be effected has been shown repeatedly throughout the investigation by the absorption

of oxygen volumes during revivification equivalent to the hydrogen previously absorbed.

The ability of the reagent to be completely revivified suggests the possibility of a long life. Of the solutions so far prepared, all but two have been removed from operation in order to recover the palladium for use with other preparations and for no other reason. The two exceptions suffered loss of activity due to precipitation of the palladium by excessive temperatures purposely used during the study of the variation of activity with temperature. It so happened that these solutions (C and D) were subjected to the greatest number of hydrogen absorption tests. Solution C, whose volume was 120 cc., absorbed a total volume of 2708 cc. Prior to the drop in activity at elevated temperature, 2250 cc. of hydrogen had been absorbed with no loss in activity. The loss of activity after the absorption of 2708 cc. amounted to 10 per cent.

Solution D, whose volume was 120 cc., had absorbed a volume of 2860 cc. before it was subjected to excessive temperature with a resulting loss of activity. However, after the precipitated palladium colloid was filtered out and replaced by fresh colloid, the solution was continued in use, and absorbed approximately 2000 cc. more of hydrogen.

Although the effect of long standing has not been thoroughly studied, a comparatively inactive solution (solution A) had stood from January 9 to September 20 without apparent loss of activity or precipitation of the colloid.

Application of Reagent to Standard Gas Analysis Practice

Activity of Reagent in a Standard Size Pumping Pipet. With the standard 200-cc. automatic pumping pipet the activity of the reagent is somewhat increased, owing to the greater surface exposed. Thus, with pure hydrogen the value of the maximum absorption rate for solution C is 14.5 cc. per minute in comparison to 10.8 cc. per minute with the small pipet employed in most of the activity tests.

Use in Routine Gas Analysis. From this investigation the anthraquinone–palladium colloid reagent appears, at present, to offer a satisfactory method for the determination of hydrogen in routine gas analysis. Its use may be limited to some extent, however, by the type of apparatus employed: It would probably not be applied to apparatus of the Bureau of Mines type equipped with copper oxide tube, as this apparatus would require the addition of at least two extra pipets, one for the hydrogen reagent and one, or perhaps two, for the carbon monoxide reagent. From the standpoint of both time and accuracy it would be undesirable to restrict the use of the copper oxide tube in this apparatus to the determination of carbon monoxide.

The application of this reagent seems feasible with apparatus of the types of the United States Steel Corporation, Bone and Wheeler, the Elliott, the Illinois modification of the Morehead (equipped with slow combustion pipet), Hempel, Sheppard, and the Bureau of Mines type equipped with the extra absorption pipets and without the copper oxide tube. In the analysis of gases of low hydrogen and carbon monoxide content, the use of this reagent appears to be preferred to the fractionation over copper oxide.

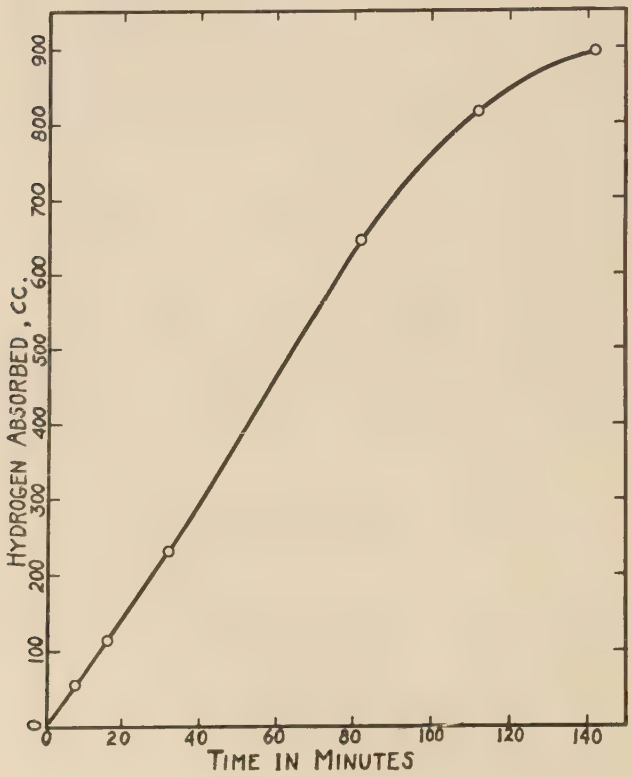

FIGURE 5. HYDROGEN ABSORPTION CAPACITY OF REAGENT, SOLUTION C

Further Development

In order to be economic the methods of preparation should be reduced to a production routine and, if possible, simplified. An investigation of the effect of the variation in alkalinity must be carried out. It appears that the hydrogen-ion concentration controls to a marked degree the rate of absorption of both hydrogen and oxygen and the tendency of the reagent to foam. An increase in the foaming tendency with use was attributed to the absorption of carbon dioxide from the

air with accompanying increase in hydrogen-ion concentration. Upon addition of a small amount of sodium hydroxide, no foaming occurred. In the case of the two most active reagents, solutions C and H, the foam broke immediately upon stopping the pumping action.

Summary

The literature concerning the various liquid reagents which have been proposed for the determination of hydrogen has been reviewed and a brief criticism of such methods has been made.

A new reagent has been developed, consisting of an aqueous solution of sodium anthraquinone 2,7-disulfonate and colloidal palladium peptized by an alkaline albumin compound, sodium protalbinate. This reagent has the advantage of being readily revivified by contact with oxygen or air, assuring active hydrogen absorption over long periods of operation.

The characteristics of the reagent, with particular reference to its application to routine gas analysis, have been studied and may be summarized as follows:

1. The reagent is more active than any liquid reagent tested by the authors for the determination of hydrogen. With pure hydrogen the absorption rate, in a suitable gas-analysis pipet, is about 15 cc. per minute.
2. The reagent operates satisfactorily at room temperature.
3. Hydrogen may be determined accurately in the presence of nitrogen and saturated hydrocarbons. The absorption is complete.
4. In routine analysis carbon dioxide, unsaturates, oxygen, and carbon monoxide should be removed prior to the hydrogen determination.
5. Although temporarily poisoned by carbon monoxide and carbon disulfide, the reagent regains its activity upon standing in contact with oxygen or air.
6. Hydrogen and oxygen may be removed simultaneously.
7. The reagent appears to remain active after standing several months and appears to be unaffected by light.
8. The capacity is sufficient to care for a number of determinations before revivification becomes necessary. The spent reagent is completely and simply revivified by contact with air or oxygen.

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BIOGRAPHY

Donald Theodore Bonney, son of James H. and Mary (Pettibone) Bonney, was born in Union City, Erie County, Pennsylvania, on March 21, 1904. He attended the grade and high schools of Edgewood, Pittsburgh, Pennsylvana, and the Baltimore Polytechnic Institute, from which he was graduated in June, 1923. He entered the Johns Hopkins University in September, 1923, and received the degree of Bachelor of Engineering in Gas Engineering in June, 1926.

As Research Assistant in Gas Engineering at the Johns Hopkins University, from September, 1926, to September, 1933, he was engaged in the investigation of synthetic liquid fuels from commercial gases and of the removal of sulfur compounds from gas. During this period he also attended certain graduate courses. Upon his resignation as Research Assistant in September, 1933, he devoted the academic years 1933–34 and 1934–35 to study for an advanced degree. In addition to his regular graduate work he served as Junior Instructor in Gas Engineering from January, 1934 to January, 1935. He is at present serving as Research Assistant in that Department.

He is a member of the American Chemical Society and Sigma Xi.